United States Patent [19]

Karrer

[11] **4,080,470**

[45] **Mar. 21, 1978**

[54] **(4-PHENOXY)-PHENOXY-ALKYL(OR CYCLOHEXYL) CARBAMATES**

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[30] **Foreign Application Priority Data**

Aug. 22, 1975 Switzerland 10902/75
Jul. 16, 1976 Switzerland 9137/76

[51] **Int. Cl.**[2] **C07C 125/06;** A01N 9/24

[52] **U.S. Cl.** ..... **424/300;** 260/463; 260/613 R; 560/164; 71/106

[58] **Field of Search** ..... 260/482 C; 424/300; 560/164

[56] **References Cited**

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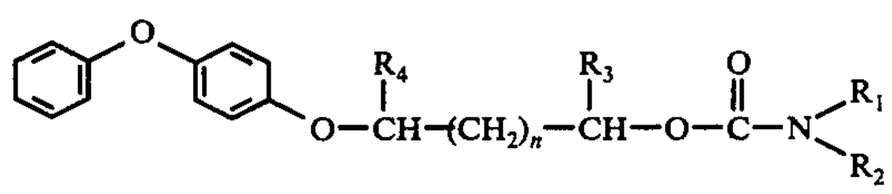
[57] **ABSTRACT**

New carbamates of the formula



(I),

are disclosed,

wherein

R_1 represents an alkyl group having 1 to 4 carbon atoms, a haloethyl group or an alkenyl group having 3 to 4 carbon atoms,

each of R_2 and R_3 represents a hydrogen atom, a methyl or ethyl group,

R_4 represents a hydrogen atom or a methyl group or

R_3 and R_4, if n is O, together represent the radical $—CH_2—CH_2—CH_2—CH_2—$, and

n is O, 1 or 2.

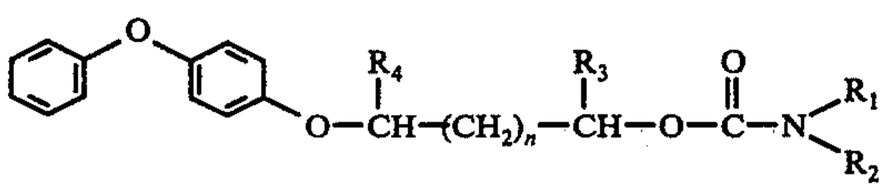
These compounds are useful as pesticides, especially for the control of insects and pests of the order Acarina; they are also useful for regulating plant growth.

16 Claims, No Drawings

(4-PHENOXY)-PHENOXY-ALKYL(OR CYCLOHEXYL) CARBAMATES

The present invention provides new carbamates, a process for their manufacture and a method of using them in pest control and for regulating plant growth.

The carbamates of this invention have the formula I



(I),

wherein

R_1 represents an alkyl group having 1 to 4 carbon atoms, a haloethyl group or an alkenyl group having 3 to 4 carbon atoms,

each of R_2 and R_3 represents a hydrogen atom, a methyl or ethyl group,

R_4 represents a hydrogen atom or a methyl group or

R_3 and R_4, if n is 0, together represent the radical —CH_2—CH_2—CH_2—, and

n is 0, 1 or 2.

Haloethyl is to be understood in particular as meaning chloroethyl.

The alkyl and alkenyl groups represented by R_1 can be straight-chain or branched. Examples of such groups are: methyl, ethyl, propyl, isopropyl, n-butyl, iso-butyl, sec. and tert. butyl, and allyl.

Preferred compounds on account of their action are those of the formula I, wherein R_1 represents a methyl, ethyl or allyl group, R_2 represents a hydrogen atom, a methyl or ethyl group, each of R_3 and R_4 represents a hydrogen atom or a methyl group, but preferably a hydrogen atom, and n is 0 or 1, preferably 0.

The compounds of the formula I are obtained by methods which are known per se, for example as follows:

In the formulae (II) to (VIII), the symbols R_1, R_2, R_3, R_4 and n are as defined for formula (I) and X represents halogen, in particular a chlorine or bromine atom.

Examples of suitable bases are tertiary amines, such as trialkylamines. In process B, catalytic amounts of 1,4-diazabicyclo-(2,2,2)octane for example or tertiary amines are added. Processes A, B and C are carried out at a reaction temperature of −5° to +120° C (process A preferably in the temperature range from 10° to 110° C, process B from 10° to 90° C, and process C from 10° to 60° C), at normal pressure and in the presence of inert solvents and diluents.

Examples of suitable solvents or diluents are: hydrocarbons, such as benzene, toluene, hexane, heptane; ethers, such as diethyl ether, dimethoxyethane, dioxane; pyridine, and esters, for example ethyl acetate.

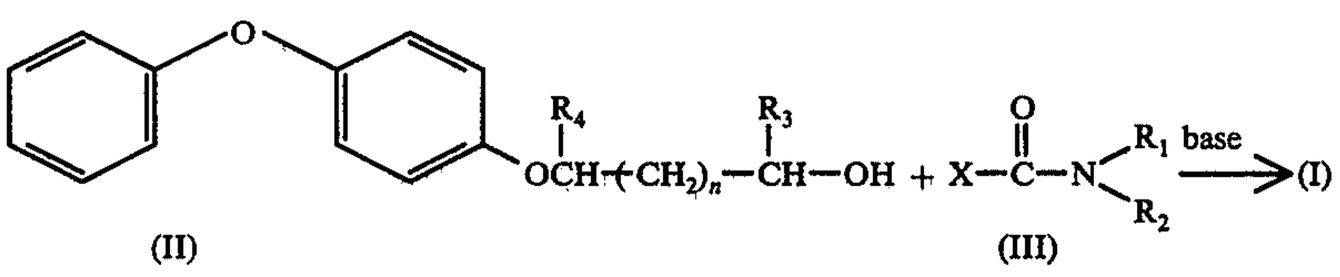
The starting materials of the formulae II and V are known compounds or they can be prepared analogously to known methods described in the literature.

The compounds of formula I are suitable for controlling a variety of animal and plant pests, particularly for combating members of the order Acarina of the families:

Ixodidae, Argasidae, Tetranychidae, Dermanyssidae, and insects of the families: Acrididae, Blattidae, Gryllidae, Gryllotalpidae, Terrigoniidae, Cimicidae, Pyrrhocoridae, Reduviidae, Aphididae, Delphacidae, Diaphididae, Pseudococoidae, Chrysomilidae, Coccinellidae, Bruchidae, Scarabaeidae, Dermestidae, Tenebrionidae, Curculionidae, Tineidae, Noctuidae, Lymantriidae, Pyralidae, Galleridae, Culicidae, Tipulidae, Stomoxydae, Muscidae, Galliphoridae, Trypetidae, Pulicidae. The compounds of formula I are also suitable for regulating plant growth, for example as fruit abscission agents.

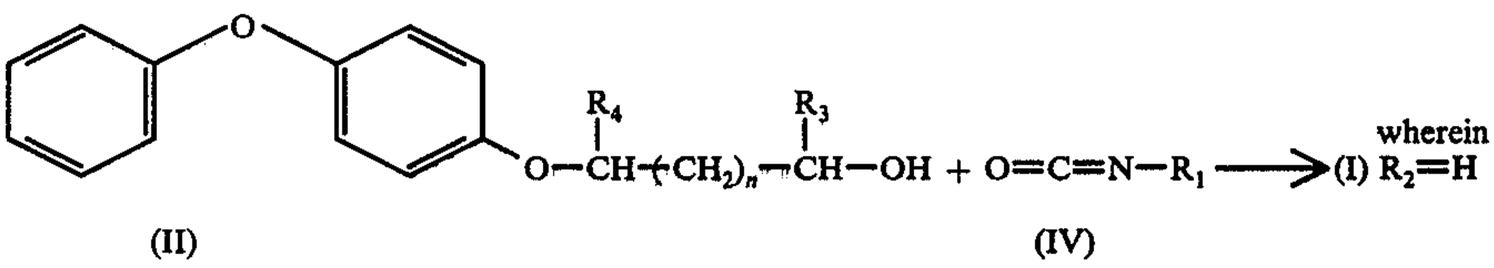
The pesticidal action can be substantially broadened and adjusted to prevailing conditions by adding other insecticides and/or acaricides.

A)



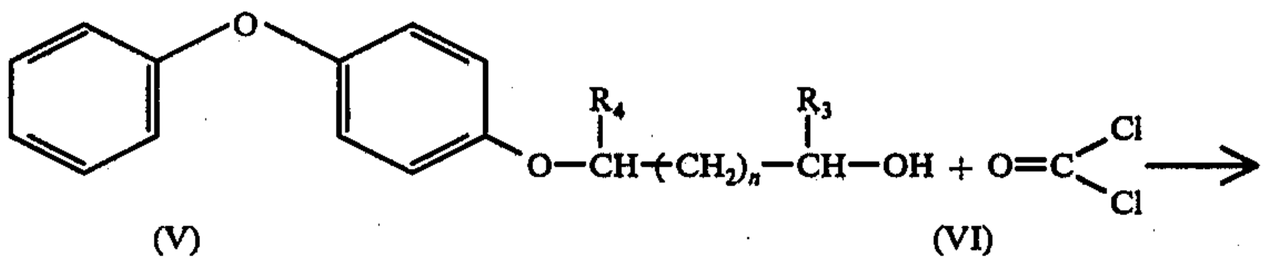
(II) (III)

B)

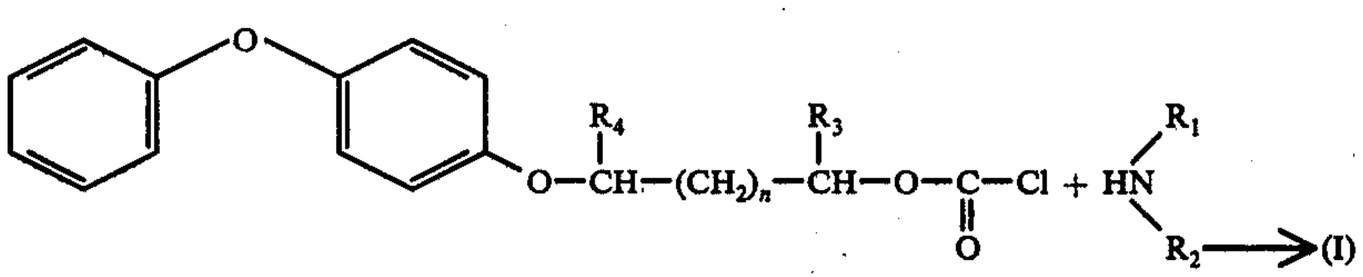


(II) (IV)

C)



(V) (VI)



(VII) (VIII)

Examples of suitable additives are: organic phosphorus compounds, nitrophenols and their derivatives; formamidines, ureas, carbamates, chrysanthemum acid derivatives, or chlorinated hydrocarbons.

The compounds of formula I can be used as pure active substance or together with suitable carriers and/or additives. Suitable carriers or additives may be solid or liquid and correspond to the substances conventionally used in the art of formulation, for example: natural and regenerated substances, solvents, dispersing agents, wetting agents, stickers, thickeners, binders or fertilizers.

For application, the compounds of formula I can be processed to dusts, emulsion concentrates, granulates, dispersions, sprays, to solutions or suspensionsin formulations well known to those skilled in the art of application.

The compositions of the present invention are obtained in known manner by intimately mixing and/or grinding active substances of formula I with suitable carriers, with or without the addition of dispersants or solvents which are inert to the active ingredients. The active substances can be applied in the following application forms.

Solid preparations: dusts, tracking agents, granulates (coated granulates, impregnated granulates and homogranulates).

LIQUID PREPARATIONS

(a) water-dispersible active substance concentrates: wettable powders, pastes or emulsion;
(b) solutions.

The content of active substance in the compositions described above is between 0.1 and 95 percent by weight.

The active substances of formula I can be formulated for example in the following way:

DUSTS

The following substances are used for the preparation of (a) a 5% (b) a 2% dust:

(a)
5 parts of active substance
95 parts of talcum

(b)
2 parts of active substance
1 part of highly dispersed silicic acid
97 parts of talcum

The active ingredients are mixed and ground with the carriers.

GRANULATES

The following substances are used to obtain a 5% granulate:
5 parts of active substance
0.25 parts of epichlorohydrin
0.25 parts of cetyl polyglycol ether
3.50 parts of polyethylene glycol
91 parts of kaolin (particle size 0.3–0.8 mm).

The active substance is mixed with epichlorohydrin and dissolved in 6 parts of acetone, then the polyethylene glycol and cetyl polyglycol ether are added. The resultant solution is sprayed onto kaolin and the acetone is subsequently evaporated in vacuo.

WETTABLE POWDER

The following ingredients are used to prepare: (a) a 40%, (b) and (c) a 25% and (d) a 10% wettable powder.

(a)
40 parts of active substance,
5 parts of sodium lignin sulphonate,
1 part of sodium dibutyl-naphthalenesulphonate,
54 parts of silicic acid;

(b)
25 parts of active substance,
4.5 parts of calcium lignin sulphonate,
1.9 parts of Champagne chalk/hydroxyethyl cellulose mixture (1:1),
1.5 parts of sodium dibutyl naphthalenesulphonate,
19.5 parts of silicic acid,
19.5 parts of Champagne chalk,
28.1 parts of kaolin;

(c)
25 parts of active substance,
2.5 parts of isooctylphenoxy-polyoxyethyleneethanol,
1.7 parts of Champagne chalk/hydroxyethyl cellulose mixture (1:1),
8.3 parts of sodium aluminium silicate,
16.5 parts of infusorial earth,
46 parts of kaolin;

(d)
10 parts of active substance,
3 parts of a mixture of the sodium salts of saturated fatty alcohol sulphates,
5 parts of naphthalenesulphonic acid/formaldehyde condensate,
82 parts of kaolin.

The active substances are intimately mixed in suitable mixers with the additives, and the mixture is then ground in appropriate mills and rollers. Wettable powders are obtained which can be diluted with water to give suspensions of any desired concentration.

EMULSIFIABLE CONCENTRATES

The following substances are used to produce (a) a 10%, (b) a 25%, and (c) a 50% emulsifiable concentrate:

(a)
10 parts of active substance,
3.4 parts of epoxidised vegetable oil,
3.4 parts of a combination emulsifier consisting of fatty alcohol polyglycol ether and alkylarylsulphonate calcium salt,
40 parts of dimethyl formamide,
43.2 parts of xylene;

(b)
25 parts of active substance,
2.5 parts of epoxidised vegetable oil,
10 parts of alkylarylsulphonate/fatty alcohol polyglycol ether mixture,
5 parts of dimethyl formamide,
57.5 parts of xylene;

(c)
50 parts of active substance,
4.2 parts of tributylphenol-polyglycol ether,
5.8 parts of calcium-dodecylbenzenesulphonate,
20 parts of cyclohexanone,
20 parts of xylene.

By diluting these concentrates with water it is possible to obtain emulsions of any required concentration.

SPRAY

The following ingredients are used to prepare (a) a 5% spray, and (b) a 95% spray:

(a)
5 parts of active substance,

1 part of epichlorohydrin,
94 parts of ligroin (boiling range 160°–190° C);
(b)
95 parts of active substance,
5 parts of epichlorohydrin.

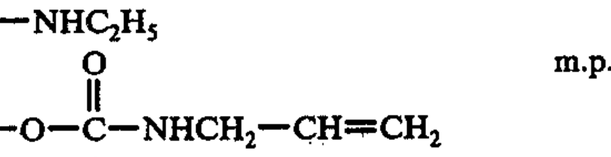
The invention is further illustrated by the following Examples.

EXAMPLE 1

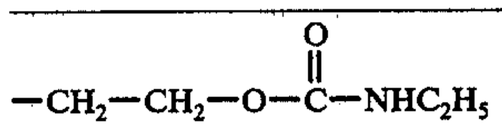
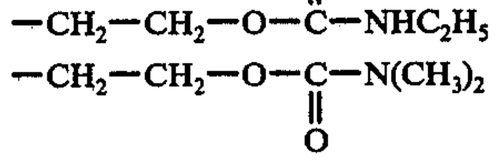
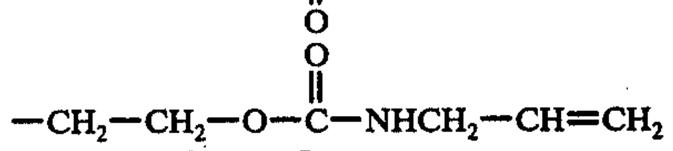
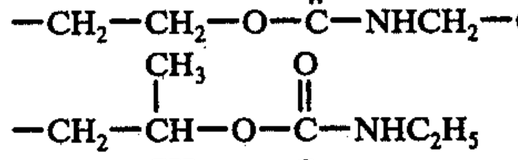
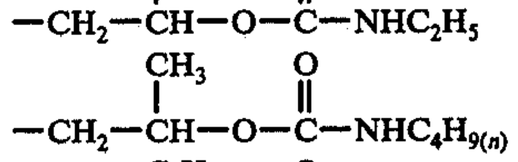
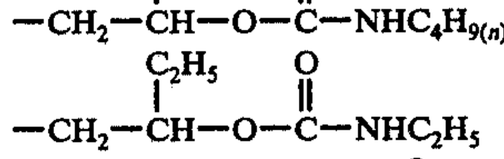
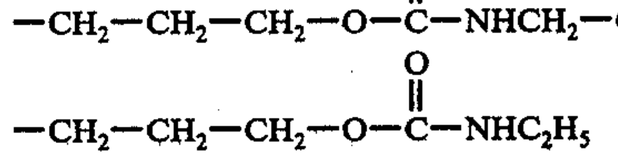
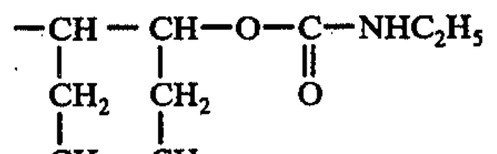
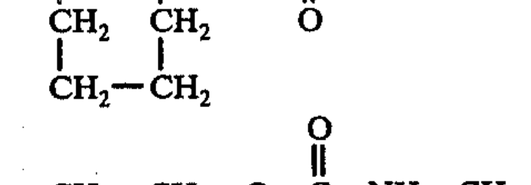
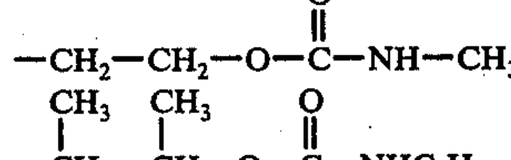
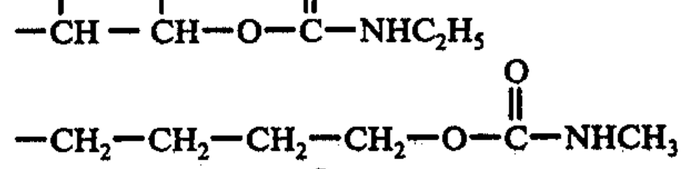
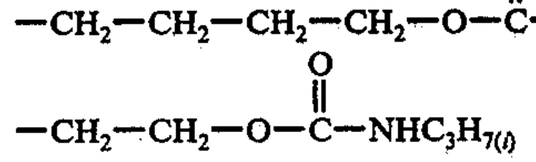
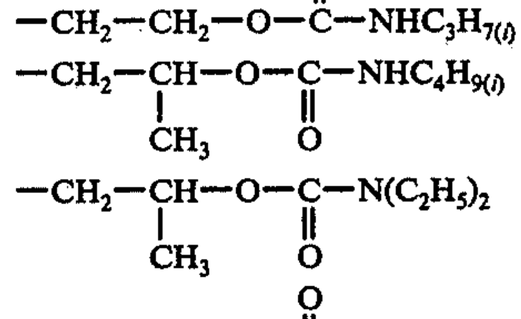
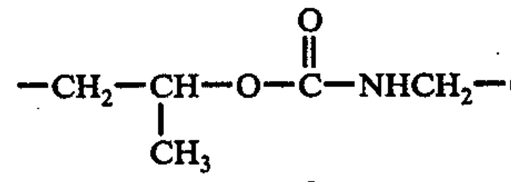
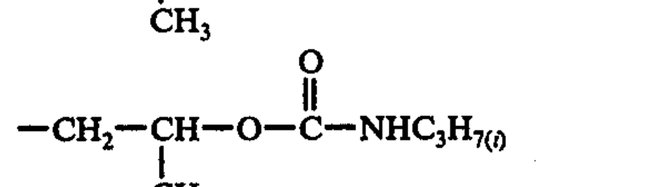
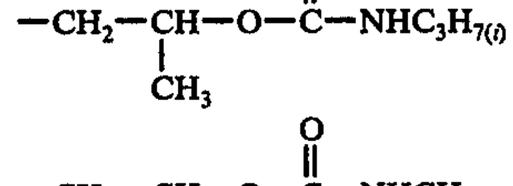
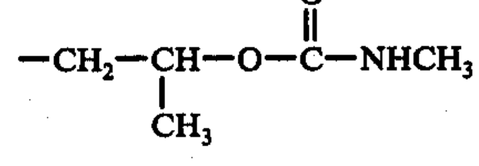
Preparation of
2-(4-phenoxy)-phenoxy-ethane-N,N-diethylcarbamate

To a solution of 34.5 g of 2-(4-phenoxy)-phenoxy-ethanol (m.p. 63°–64° C) in 200 ml of anhydrous toluene are added, with stirring, 16.8 g of triethylamine and 22.4 g of N,N-diethylcarbamoyl chloride, and the reaction mixture is heated for 72 hours to 110° C. The reaction mixture is worked up by cooling it to room temperature and washing it repeatedly with water, 0.5 normal hydrochloric acid and finally with a saturated solution of sodium chloride. The organic phase is dried over sodium sulphate, then the solvent is distilled off in vacuo and the residue is recrystallised from isopropanol to yield 2-(4-phenoxy)-phenoxy-ethane-N,N-diethylcarbamate with a melting point of 77°–78° C.

The following compounds of the invention of formula IX


(IX)

are also obtained in analogous manner:

R′	Physical data
	m.p.: 55–56° C
	m.p.: 54–55° C
	m.p.: 51–52° C
	m.p.: 62–63° C
	m.p.: 59–60° C
	m.p.: 61–62° C
	m.p.: 42–43° C
	m.p.: 42–43° C
	m.p.: 90–91° C
	m.p.: 63–64° C
	m.p.: 72–73° C
	m.p.: 77–79° C
	m.p.: 68–69° C
	m.p.: 71–72° C
	n_D^{20}: 1,5358
	n_D^{20}: 1,5534
	m.p.: 74–75° C
	n_D^{20}: 1,5522

-continued

R′	Physical data
$-CH_2-CH_2-O-\overset{\overset{O}{\|}}{C}-NH-CH_2-CH=CH-CH_3$	m.p.: 61–63° C
$-CH_2-CH_2-O-\overset{\overset{O}{\|}}{C}-NH-CH_2-CH_2-Cl$	n_D^{20}: 1,5387
$-CH_2-CH_2-CH_2-O-\overset{\overset{O}{\|}}{C}-N(C_2H_5)_2$	m.p.: 69–70° C
$-CH_2-CH_2-O-\overset{\overset{O}{\|}}{C}-NH-C_4H_9(tert.)$	

EXAMPLE 2

(A) Contact action on Dysdercus fasciatus larvae

A specific amount of a 0.1% solution of active compound in acetone (corresponding to 10 mg active substance/m^2) was pipetted into an aluminum dish and distributed homogeneously.

After evaporation of the acetone, 10 larvae of Dysdercus fasciatus in the fifth stage were put into the dishes containing feed and moist cotton wool. The dish was then covered with a perforated top.

After about 10 days, i.e., after the untreated controls had shed and emerged fully to the adult stage, the treated test subjects were examined for the number of normal adults.

The compounds of formula I displayed good activity in the above test.

(B) Contact action on Tenebrio molitor pupae

A specific amount of a 0.1% solution of active substance in acetone, corresponding to 10 mg active substance/m^2, was pipetted into an aluminum dish and homogeneously distributed.

After evaporation of the acetone, 10 pupae which had just shed their cocoon were placed onto the treated plate. The dish was covered with a perforated top.

After the untreated controls had emerged from the pupae cocoon as imagines, the test subjects were examined for the number of adults.

The compounds of formula I showed good activity in the above test.

EXAMPLE 3

Action on Musca domestica

50 g of freshly prepared CSMA nutrient substrate for maggots were charged into beakers. A specific amount of a 1% acetonic solution of the respective active substance was pipetted onto the nutrient substrate present in the beakers. The substrate was then thoroughly mixed and the acetone subsequently allowed to evaporate over a period of at least 20 hours.

Then 25 one day-old maggots of Musca domestica were put into each of the beakers containing the treated nutrient substrate for testing with each active substance at one of its given concentrations. After the maggots had pupated, the pupae were separated from the substrate by flushing them out with water and then deposited in containers closed with a perforated top.

Each batch of flushed out pupae was counted to determine the toxic effect of the active substance on the maggot development. The number of flies which had hatched out of the pupae was then counted after 10 days and any influence on the metamorphosis thereby determined.

The compounds of the formula I displayed good activity in this test.

EXAMPLE 4

Action on ticks

(A) Rhipicephalus bursa

5 adult ticks and 50 tick larvae were counted into each of a number of test tubes and immersed for 1 to 2 minutes in 2 ml of an aqueous emulsion containing a concentration of 100, 10, 1 or 0.1 ppm of test substance of formula I. The tube was then sealed with a cotton wool plug and placed on its head to enable the cotton wool to absorb the emulsion of the active substance.

The adults were evaluated after 2 weeks and the larvae after 2 days. Each test was repeated twice.

(B) Boophilus microplus (larvae)

20 sensitive and 20 OP-resistant larvae were tested in a dilution series analogous to the one used in test A. (the resistance refers to the tolerance towards diazinone).

The substances of formula I acted in these tests on adults and larvae of Rhipicephalus bursa and OP-sensitive and OP-resistant larvae of Boophilus microplus.

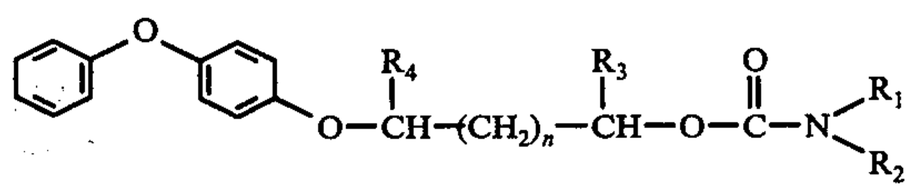
EXAMPLE 5

Action on eggs of Spodoptera littoralis

Eggs of Spodoptera littoralis were immersed in a 0.05% solution of active compound in acetone. The treated eggs were then kept in plastic dishes at 21° C and 60% relative humidity. After 3 to 4 days the hatching out rate was determined. Compounds of formula I acted well on eggs of Spodoptera littoralis in this test.

What is claimed is:

1. A compound of the formula I



(I),

wherein

R_1 represents an alkyl group having 1 to 4 carbon atoms, a chloroethyl group or an alkenyl group having 3 to 4 carbon atoms,

each of R_2 and R_3 represents a hydrogen atom, a methyl or ethyl group,

R_4 represents a hydrogen atom or a methyl group or R_3 and R_4, if n is 0, represent the radical $—CH_2—CH_2—CH_2—CH_2—$, and n is 0, 1 or 2.

2. A compound according to claim **1**, wherein n is 0.

3. A compound according to claim **1**,

wherein

R_1 represents an alkyl group having 1 to 4 carbon atoms or an allyl group,

R_2 and R_3 represent a hydrogen atom, a methyl or ethyl group,

R_4 represents a hydrogen atom or a methyl group and

n is 0, 1 or 2.

4. A compound according to claim **3**, wherein

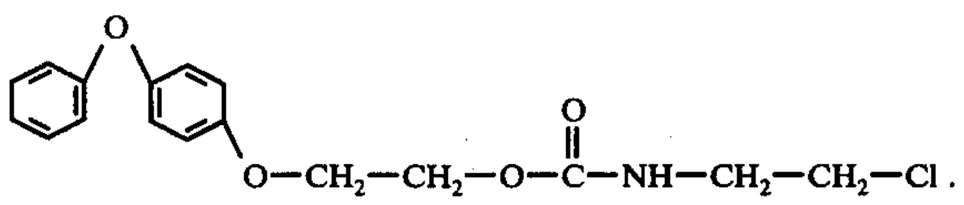
R_1 represents a methyl, ethyl or allyl group,

R_2 represents a hydrogen atom, a methyl or ethyl group,

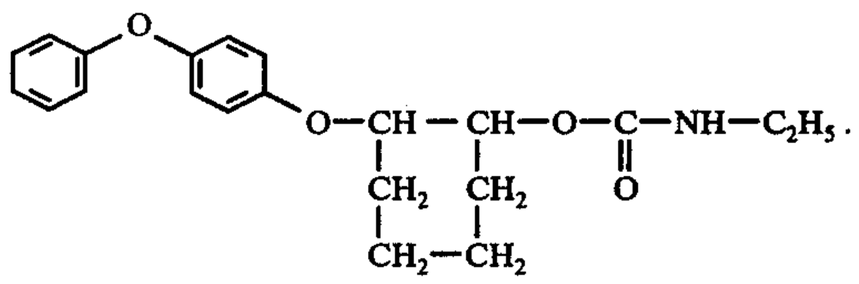
each of R_3 and R_4 represents a hydrogen atom or a methyl group and

n is 0 or 1.

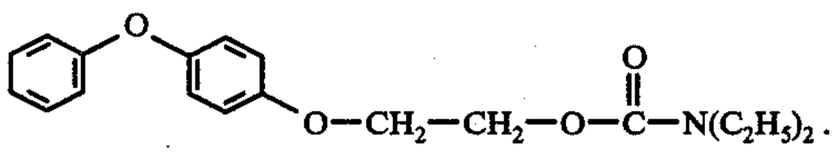
5. The compound according to claim **1** of the formula



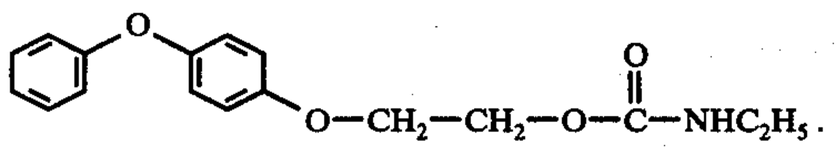
6. The compound according to claim **1** of the the formula



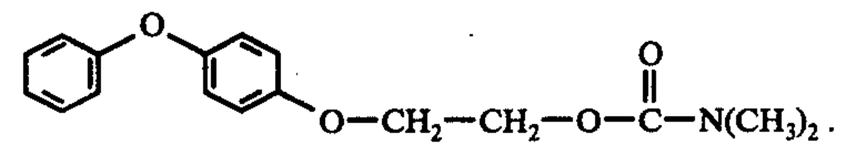
7. The compound according to claim **4** of the formula



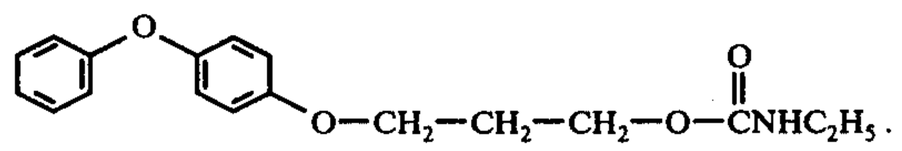
8. The compound according to claim **4** of the formula



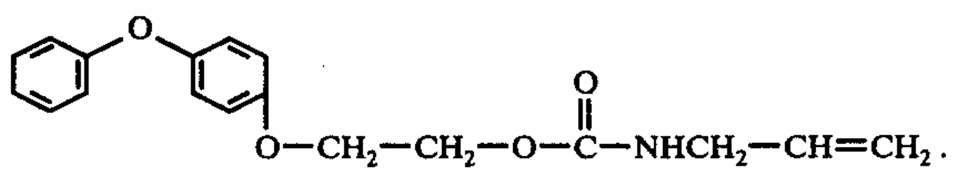
9. The compound according to claim **4** of the formula



10. The compound according to claim **4** of the formula



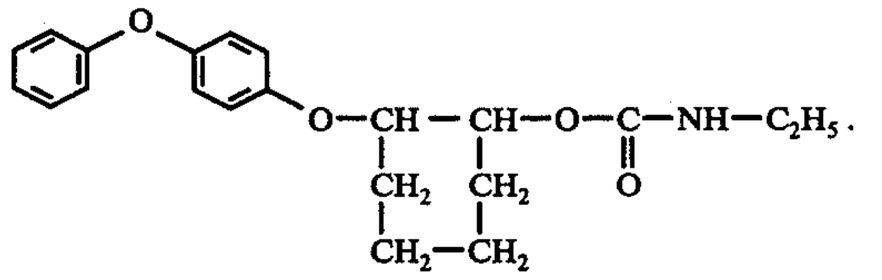
11. The compound according to claim **4** of the formula



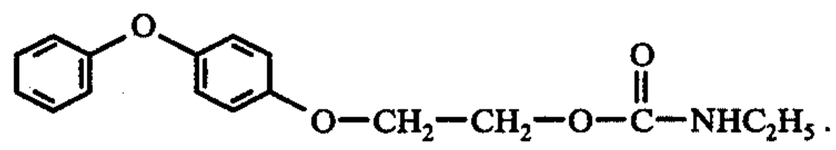
12. An insecticidal and acaricidal composition comprising an insecticidally and acaricidally effective amount of a compound according to claim **1** together with a suitable carrier therefor.

13. A method for combatting insects and acarids which comprises applying thereto or to the locus thereof an insecticidally and acaricidally effective amount of a compound according to claim **1**.

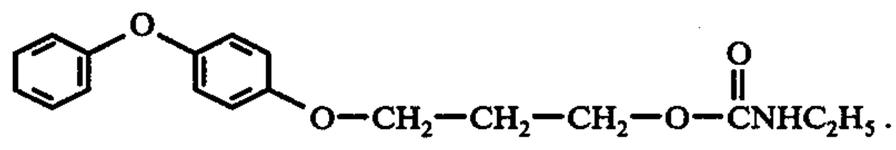
14. The method of claim **13**, wherein said compound corresponds to the formula



15. The method of claim **13**, wherein said compound corresponds to the formula



16. The method of claim **13**, wherein said compound corresponds to the formula



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